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On the Thermodynamics of Solar Energy Use

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ON THE THERMODYNAMICS OF SOLAR ENERGY USE

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ABSTRACT — Solar energy, coming from a 5800K heat reservoir, has thermodynamic advantages over fossil fuel combustion which are rarely recognized. This essay discusses the pertinent thermodynamics of chemical conversion processes. It points out the advantage of conducting endothermic processing at high temperatures and the unique character of sunlight as a source of process heat for high-temperature processing.

Most of us associate solar energy use with hot water and comfort heating. That's good! The rising cost of fuel may make it compelling someday, even in places that do not have as high an insolation as Israel, where about 80% of the domestic hot water is solar heated.

But, from a thermodynamic standpoint, such uses of sunlight are inelegant. Solar energy offers earthlings unique opportunities because its source is a high-temperature reservoir.

The second law of thermodynamics legislates a unidirectionality to the flow of things in nature. In the absence of external agents such as refrigerating machines using external power supplies, energy *as heat* flows only from warmer places to cooler ones. We can, in principle, use all of the energy we extract from one place *as work* to raise the temperature of ("heat up") another object, no matter how high its temperature. But we can never use all of the energy we extract from a place *as heat* to do work. Moreover, if we don't have a cooler place to which that fraction of the energy which *isn't* used to do work can flow spontaneously, we can't use heat to do any work at all.

Carnot was the first to point out that cyclic heat engines could use at best only a fraction of the energy they might extract from a heat source to do useful work. The highest such fraction, the efficiency of a Carnot heat engine, is $(T_h - T_l)/T_h$, where T_h and T_l are the temperatures of the engine's source and sink, respectively. No part of the engine can be heated to a temperature higher than T_h or cooled to a temperature lower than T_l. In practice, even with perfect engines, T_h and T_l become the highest and lowest temperatures in the engine, regardless of the source and sink temperatures.

The sun is a 5800K source. With the earth, a 300K object, as a sink, we should in principle be able to convert about 0.95 of incoming sunlight into useful work. That is the theoretical limit for all devices, including perfect so-called quantum devices such as photovoltaic devices. An ideal heat engine would achieve 90% of that efficiency if the highest temperature in its cycle were only about 2050K. It therefore behooves us to explore the possibility of using sunlight in ways which take advantage of its inherent thermodynamic value.

In using sunlight as a low temperature source, we limit our options. In using it as a high temperature source to do work or its equivalent, we provide ourselves with many options for using it, including the option of providing low temperature comfort heat.

If we store it as potential energy by requiring it to do the work of charging a storage battery, for example, we can use it later to operate lights or machines for making useful things in the building, concurrently providing comfort heat. Or, we might have used it to cool the building instead.

If we do not use it to do useful work as we receive it from the sun, but simply permit it to warm up the building or heat water in a storage tank, we will have lost *forever* most of that sunlight's capacity for doing useful work. That may not be bad, especially if the capital cost of using it that way is low and the cost of fuel is high, but it is inelegant.

But, because the sun *is* a unique source, it can do some things that terrestrial fuels can't do and others more efficiently. The highest temperatures we can achieve in burning fuels in air are about 2300K. We can't get much high-temperature process heat by combustion alone. When we need it we must convert some of the energy of the fuel-air system to electric power to use with a resistance heater or an arc, accepting a certain amount of complication with its concomitant losses.

But the sunlight that reaches the earth is still energy from a 5800K source. By concentrating it in such a way as to reconstitute an image of the sun on earth, we can use it to provide process heat at temperatures which are limited only by the temperature of the sun and the quality of our optical devices.

Earthly Objectives

In pursuing earthly objectives, we almost always start out with available materials at ambient temperature and pressure, do something such as extract a metal from an ore, generate electric power, manufacture a particular substance using the raw materials we find in nature, or run fuel and air through an internal combustion engine to make the engine do work, and then return the products to the same ambient conditions.

It is often instructive to represent these processes as having taken place in a system, a black box, which takes in reactants and exhausts products at ambient conditions while exchanging heat and work with the surroundings. For our purposes, the surroundings may include the sun.

An Example Chemical Transformation

Suppose our objective is to decompose water into hydrogen and oxygen. We propose to do it in the water-splitting device represented in Figure 1. The first mechanism that comes to the minds of many of us is an electrolysis cell. That might be a good device to use if wind or hydroelectric power were among the prime energy sources available to us. But electric power must usually be manufactured from primitive materials, fuels which are processed in such a way as to create heat reservoirs. Thus, the power plant must be included in the black box as one of the components of our water-splitting device. It may, however, use materials or heat from outside sources.

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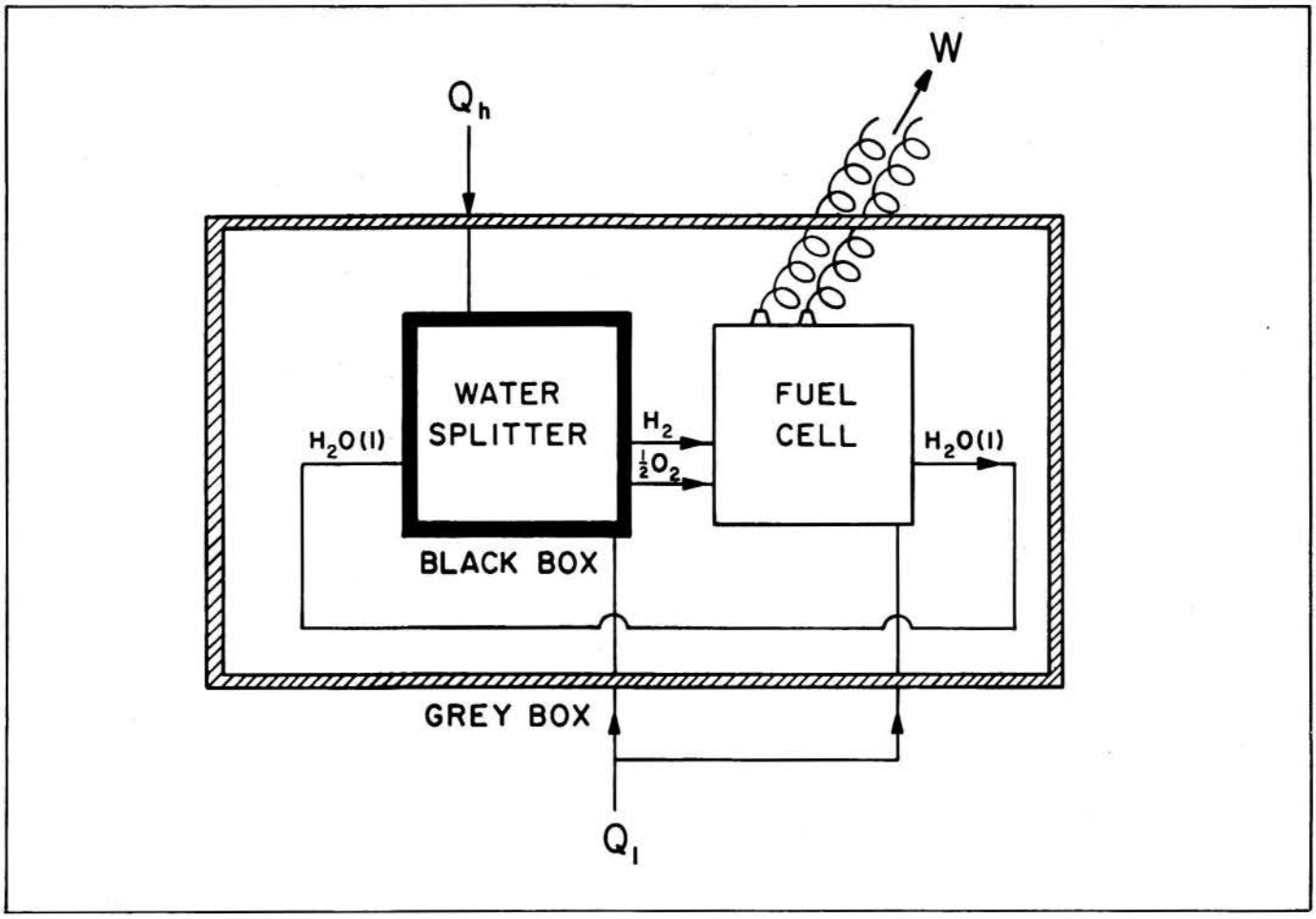

Figure 1. The reactor (the black box) is a device which receives ambient temperature and pressure liquid water and can exchange heat with either the high- or the ambient-temperature reservoir. The reactor product is ambient temperature and pressure hydrogen and oxygen. The reactor is the device whose performance we are interested in. The fuel cell is an intellectual construct we use for the purpose of understanding the requirements and limitations of the reactor. The electrical work of the fuel cell measures the amount of hydrogen and oxygen which have been manufactured by the reactor. When the water from the fuel cell is returned to the reactor, the system is closed. If it is conceptually enclosed within a grey boundary, the grey enclosure becomes a heat engine, viz it is a device which takes energy from a heat reservoir, does external (electrical) work, and rejects heat to a heat sink, the ambient temperature surroundings.

For the purpose of taking a first thermodynamic look at some of the limitations nature imposes on us, it is not necessary that we specify what is in the box or how it works. On the contrary, we may circumscribe our thoughts about ways of achieving our objective by being too specific at first. Our device is simply a black box that takes in liquid water at ambient temperature and pressure, exhausts an equivalent amount of separated hydrogen and oxygen, each at ambient temperature and pressure, and in the process may exchange heat with reservoirs at ambient temperature as well as at a higher temperatures.

It is easy to show from first law considerations alone that energy must be supplied to the box in the process. For the splitting of one mole of water, 285.8 kilojoules (kJ) of energy must be supplied, the enthalpy change (ΔH) of the reaction

$$H_2O\,(l,\ 1\ atm,\ 300K) \longrightarrow H_2\,(g,\ 1\ atm,\ 300K) + 0.5O_2\,(g,\ 1\ atm,\ 300K) \qquad (1).$$

That is a necessary but not sufficient condition for the occurrence of the reaction. It is evident that we cannot cause that much heat to flow to it from a 400K reservoir for the purpose of splitting water.

We could, however, use the 400K reservoir as the source for a Carnot engine, contained in the black box, which rejects heat to the 300K surroundings and reversibly generates electric power which we use reversibly to electrolyze the water at 300K. The amount of electrical work required is the Gibbs free energy change (ΔG) of Reaction 1, 237.2kJ. The Carnot engine would have a thermal efficiency of (400—300)/400 or 0.25. It takes 948.8kJ from the hot reservoir and rejects 711.6kJ to the surroundings to produce the 237.2kJ of electrical energy, required for the electrolysis, and the electrolysis cell takes up 48.6kJ as heat from its surroundings in the process. We have thus achieved our objective. Although the net flow of energy to the box was the required 285.8kJ, the real cost to us was 948.8kJ of energy taken from a 400K reservoir. If we had taken our energy from a 600K reservoir, we would have required only 474.4kJ from it.

Let us now elaborate our analysis and make it more general. We still need not be concerned with what is in the black box. We feed it heat from a hot reservoir and liquid water at ambient conditions. It gives us hydrogen and oxygen at ambient conditions. It may also exchange heat with the ambient temperature surroundings.

We now introduce as an intellectual construct, a reversible hydrogen-oxygen fuel cell, also shown in Figure 1, which can take the products from the black box, recombine them and do electrical work on the surroundings in the amount ΔG(of reaction 1) for each mole of water that has been split in the black box.

The fuel cell also exchanges heat with the ambient temperature surroundings. The fuel cell product is fed back to the black box to complete a cycle. If we enclose the black box and fuel cell within a grey boundary, we have a new device, a heat engine, the grey box. Our grey box takes heat from a high temperature source, does external work, and rejects heat to the surroundings. The fuel cell is a meter whose work output is telling us the amount of water we are splitting in the black box. As long as we continue to feed it water and heat from the hot reservoir, the black box will continue to split water for us whether we have it connected to the fuel cell or not.

Our grey-box heat engine is, at best, a Carnot engine whose sink temperature is the ambient temperature. Its efficiency, i.e. its work output divided by the heat supplied by the heat reservoir, measures how much water we split for each joule we take from the heat reservoir. A plot of the result (1) is shown in Figure 2. The efficiency of the very best thermochemical process is equal to that of a Carnot engine operating at the same upper temperature. The result might easily have been anticipated. If it were possible to operate any chemical process with an efficiency greater than that of a Carnot engine, we would have the ingredients of a perpetual motion machine.

We are now in a position to generalize: Any isothermal chemical transformation that requires energy input can be identified with a Carnot cycle (1, 2, 3, 4). Thus, the maximum conversion efficiency, based on the input of process heat, is a monotonically increasing function of the source temperature. In other words, if we can find ways of raising the temperature at which the system accepts the flow of energy as heat without introducing irreversibilities, we can decrease the amount of energy we have to supply it to acquire a given amount of product. It is up to us to exercise our ingenuity to invent a mechanism by which it can best be done (5, 6, 7, 8).

The fact that the sunlight which reaches the earth is essentially at a temperature of 5800K thus given it obvious advantages as a source of process heat.

Concentration Ratios and the Efficiency of Energy Absorption

Near the surface of the sun, about 7 x 10^5 km from its center, the intensity of the solar radiation is characteristic of that of a black body at 5800K. By the time the sunlight has reached the neighborhood of the earth, about 1.5 x 10^8km from the center of the sun, its temperature has not changed, but its intensity has been reduced by a factor of about 46,000 as a consequence of the inverse square law.

When a black cavity on the earth absorbs sunlight, its temperature goes up until it radiates at an intensity equal to that of the solar intensity it sees, about 1/46,000 of that of a black body at 5800K. Since the intensity of radiation by a black body is proportional to the fourth power of its temperature, and because of losses due to absorption and scattering in the earth's atmosphere, that happens at a temperature a little below the boiling point of water. If we superimpose two solar intensities by using mirrors or lenses, we can achieve somewhat higher temperatures. We would refer to our superimposition of two solar images as having achieved a concentration ratio of two. If we continue to superimpose solar images with mirrors or use condensing lenses to achieve higher and higher concentration ratios we can achieve higher and higher temperatures. The theoretical limiting concentration ratio is, of course, that which would produce a steady state temperature equal to that of the sun's surface, about 46,000. In practice the highest concentration ratio in solar furnaces are those which have been built by the French at Odeillo, about 16,000. These furnaces should be capable of achieving temperatures of about 4100K in suitably designed and insulated cavity receivers.

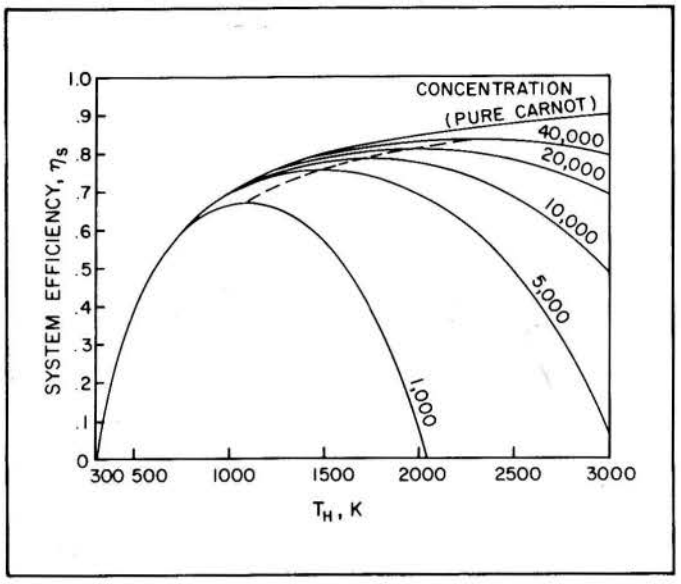

Figure 2. Variation of the system efficiencies of reversible systems with T_h. The uppermost curve is for a Carnot engine. The other curves are for devices which are otherwise reversible, but which, using the sun as a source, must necessarily reradiate energy at a rate which is proportional to the fourth power of their temperature. The parameter is concentration ratio. The dashed curve shows the maxima of the other curves (Reference 1).

When the receiver of a solar furnace is reradiating energy as fast as it is receiving it, it is at the highest temperature it is capable of achieving. The net amount of solar energy it is using is zero; its energy absorption efficiency is zero. In order use solar energy, the furnace must operate at a temperature substantially lower than the maximum it is capable of achieving.

We define the energy absorption efficiency of a solar furnace as the net rate at which energy is being absorbed in the cavity divided by the solar power incident on the area of the concentrating device. It is given by

$$\eta_c = \left(IA\eta_A\alpha - a\epsilon\sigma T_h^4 \right) / IA \qquad (2)$$

where I is the intensity of incident sunlight, A is the area of the collector normal to the direction of the sunlight, η_A is an efficiency that accounts for energy losses due to imperfections in the optical system, α and ϵ are the absorptance and emittance of the receiver, a is the reradiating area, e.g. the area of the aperture of a cavity receiver into which the concentrated sunlight is being fed, σ is the Stefan-Boltzmann constant, and T_h is the temperature in the cavity receiver. With perfect optics and a black body cavity for a receiver, this equation reduces to

$$\eta_c = \left(IC - \sigma T_h^4 \right) / IC \qquad (3)$$

where C is the solar concentration ratio appropriate to the aperture having the area a. A plot which shows the variation of the energy absorption efficiency with cavity temperature (4) for various concentration ratios is shown in Figure 3. Figure 3 shows that with a solar intensity of 1Kw per square meter, one solar intensity on the very best of days at the earth's surface, the efficiency of a black flat surface at 300K is 0.54; at 350K it is 0.15. The highest temperature we can achieve with one sun is 364K. With 100 suns it is 0.995 at 300K, and we can achieve a maximum temperature of about 1150K. With 1000 suns we can get to about 2050K; at 1500K we can absorb sunlight with an efficiency of about 0.71.

The overall efficiency of any solar thermochemical process will be the product of the solar collection efficiency and the thermal efficiency of the heat engine which correlates with the process. The maximum efficiency will therefore depend on the concentration ratio of the solar furnace and on the highest temperature used in the thermochemical process. These maximum efficiencies (1) are shown in Figure 2. It is evident that there is a thermodynamic advantage to be achieved in working with furnaces that have high concentration ratios. In the better existing furnaces, the temperature range of greatest interest lies between about 1000K and 2500K.

We have built a small research furnace at the University of Minnesota (9, Figure 4), and have measured net concentration ratios of about 7000 in it. If we could build suitable cavity receivers, we should be able to achieve temperatures in excess of 3300K in them. We are interested in working at more modest temperatures, however, so that we can use some of the energy for thermochemical processing. At 2400K, the highest temperature required for the kinds of processes we are working on now, we should be able to absorb about 0.73 of the energy that reaches the aperture.

Additional Example Applications

The kinds of processes in which there seems to be the greatest interest now are those which spawned our interest in high-temperature solar processing in the first place — those which have as their objective the storage of the ephemeral energy of the sun so that we can use it when the sun isn't shining, such as water splitting. As the feasibility of using sunlight for that purpose was explored, however, and its unique characteristics became more evident, other uses for it have emerged.

For example, hydrogen sulfide, a homologue of water, should be given serious consideration as a source of hydrogen. It is usually considered to be simply a disagreeable industrial waste product recovered in large quantities from the sweetening of fossil fuels. Some gas wells in western United States and Canada are so rich in hydrogen sulfide that they are not used. Although hydrogen sulfide itself has a reasonably high heating value, its use as a fuel is precluded by the unpleasant environmental effects that would ensue as well as by the fact that sulfur is useful for other things. Sunlight used as a source of process heat might make it worthwhile to seek and use hydrogen sulfide for its own sake as a mineral and as a heretofore untapped source of hydrogen (10).

The Claus process is now most widely used to dispose of hydrogen sulfide. The hydrogen is oxidized to water to furnish low grade process heat and sulfur is recovered. In 1979, in the United States, 1.76 million tons of sulfur was thus recovered from natural gas, and 2.31 million tons was recovered from petroleum. In Canada, 6.1 million tons was recovered.

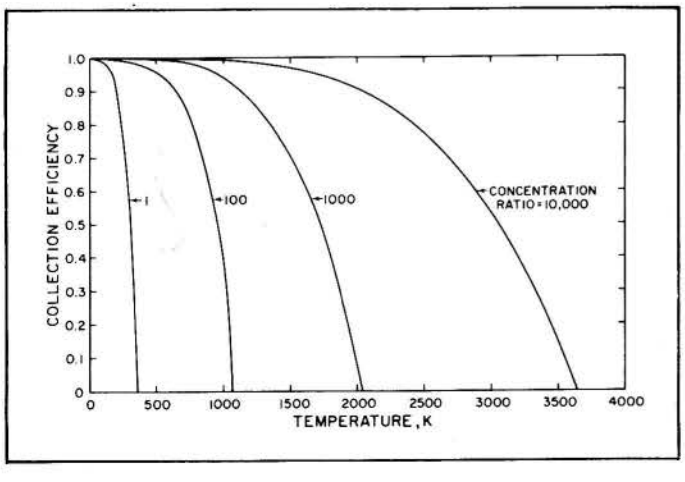

Figure 3. Variation of the energy collection efficiency of a black-body cavity receiver with its temperature, at various concentration ratios (reference 4).

The associated hydrogen might have been used to fix 2.5 million metric tons of atmospheric nitrogen as ammonia. Its heating value, 9.1 x 10^{16} J/year, 2900 megawatts, had it been recovered, would have been, in a year, equivalent to that of 17 million barrels of gasoline. Alternatively, the hydrogen might have been used to hydrogenate one million tons of coal to produce 59 million barrels of high-grade liquid hydrocarbon, about 3% of 1980 United States petroleum imports.

One estimate of the organically bound sulfur in recoverable fossil fuels in the United States alone places it at at least 40 billion metric tons. The associated hydrogen would come to about 2.7 billion tons.

A fascinating side effect of the use of hydrogen sulfide as a storage medium for solar energy is that, because the hydrogen is originally bonded much more weakly to the sulfur it is retrieved from than it is to the water it is converted to when it is used as an energy source, the input of solar energy required to produce it is, in the limit, only about one-third of the useful energy recovered when the hydrogen is finally used. For obvious reasons, however, I hesitate to call it a solar breeder reactor.

Solar energy should also be considered as a source of high-temperature process heat in electrolytic processes (11). If a chemical transformation is to take place at a given temperature and pressure, the total amount of energy which must be added to the system is the *enthalpy* change, ΔH of the reaction. However, as we have seen, it may not be possible to effect the transformation by heat addition alone. In such a situation, work may be required; energy may be added in the form of electrical work, such as is done in an electrolysis cell. The amount of electrical work needed is ΔG, the change in the *Gibbs free energy* of the chemical reaction. As electrolysis proceeds, the cell, to maintain its temperature constant, exchanges heat with the surroundings in the amount $Q = \Delta H - \Delta G$. The enthalpies and Gibbs free energies of formation of stable metallic oxides are large negative numbers. The recovery of the metal from an oxide ore at ambient or low temperatures thus requires either the use of a great deal of electric power or the use of a reducing reactant such as carbon.

The variation of ΔH of a chemical reaction with temperature depends on the difference between the heat capacities of its products and reactants, which is usually small. But the variation of the Gibbs free energy of a chemical transformation with temperature depends on the entropy change (ΔS) of the transformation, which is often a larger positive number, especially if the reactants are condensed phases and the products include gases. Thus, the enthalpies of formation of many metallic oxides (e.g. aluminum oxide) are relatively independent of temperature; their Gibbs free energies decrease with temperature. As a consequence, the electrolytic reduction of such ores at elevated temperatures requires that, as the temperature is raised, an ever-decreasing fraction of the energy required need be furnished as electric power; the rest can be process heat from a baser source.

In the Hall process for the production of aluminum from aluminum oxide, for example, process heat comes from the electric power used in excess of that which is required for electrolysis and from the combustion of the (consumable) electrodes. It is attractive to contemplate on how process heat supplied from sources other than electricity, which, from second law considerations, is energy in its most useful form, might be used to replace the consumption of this most valuable resource. The sine qua non for

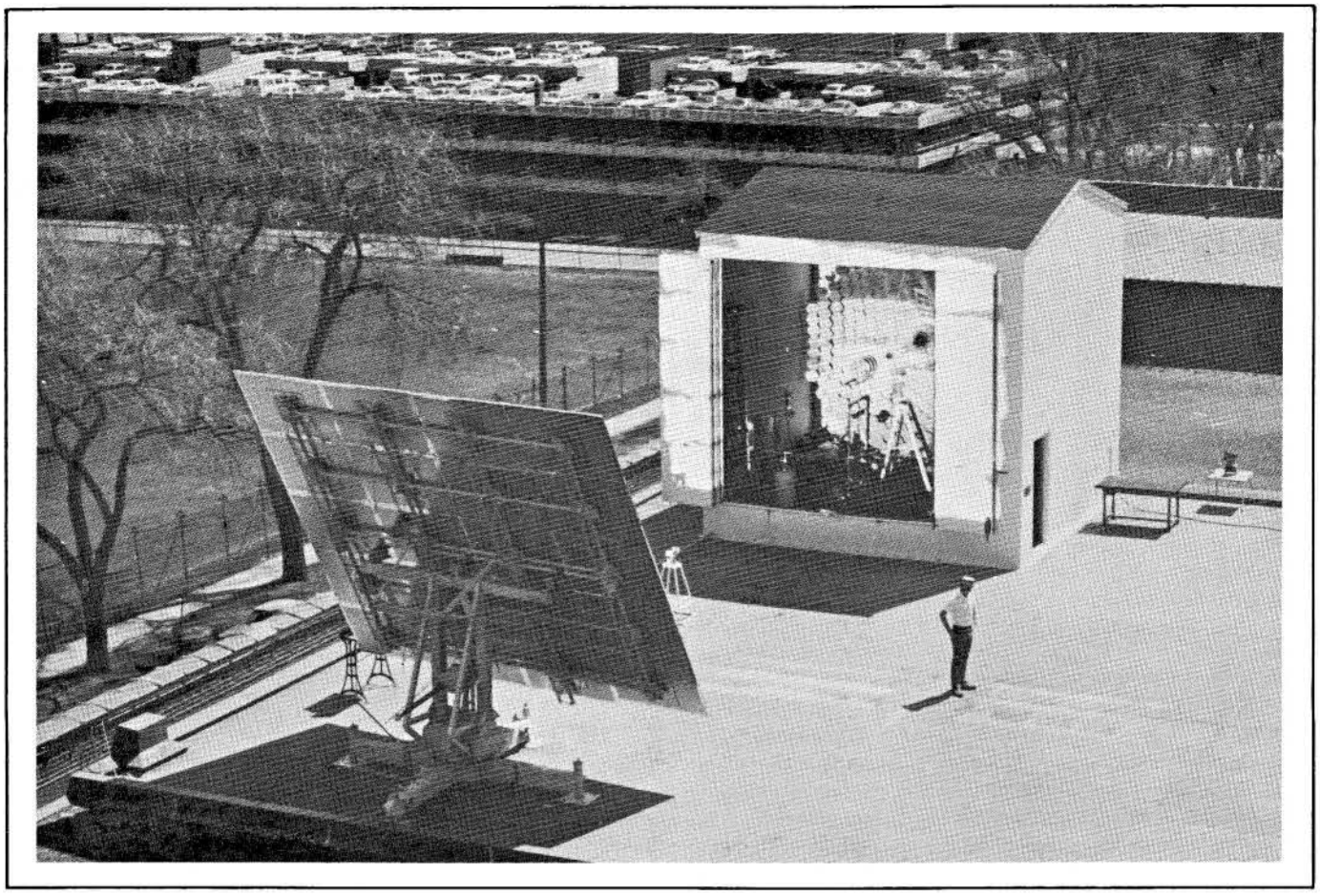

Figure 4. The 4.2 meter concentrating solar furnace of the University of Minnesota. The heliostat rotates on two axes to redirect sunlight to the concentrating array of 312 hexagonal-in-plan-form spherical mirrors whose centers are located on the surface of a sphere. The concentrating mirrors are all brought as nearly as possible to a focus at the aperture of a cavity receiver, which serves as the reactor.

such a process is a source of high-temperature process heat. The availability of high temperature process heat from sunlight suggests that its use might make high temperature electrolysis attractive for the extraction of other metals from their ores, as well as for other electrolytic processes which may be made more economical by the use of sunlight as a substitute for that portion of the electric power which would otherwise have to be used to provide process heat.

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